

*The Variation of Electrical Potential across a Semi-permeable Membrane.**

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Introduction.

It was shown by Donnan† that in certain cases the potential difference between two solutions of an electrolyte, separated by a membrane which is impermeable to the electrolyte, but permeable to the solvent, can be calculated. Thus, suppose the solutions (1) and (2)



of the electrolyte KA are separated by a membrane which does not permit the salt KA to pass, though freely permeable to other salts, with, say, the same cation K. We may then ascribe the potential difference set up at the membrane as due to the tendency of the K⁺ ions to equalise their concentrations. If we assume the permeable ions to obey the laws of ideal solutions, then

$$\pi_2 - \pi_1 = \frac{RT}{nF} \log \frac{c_1}{c_2}, \quad (\text{i})$$

where c_1, c_2 , are the molar concentrations of the K ions, n their valency, R the gas constant, F the quantity of electricity associated with a gramme-equivalent of ionic matter, and π_1, π_2 , positive potentials of the solutions. For univalent ions and 18° this reduces to $\pi_2 - \pi_1 = 0.058 \log (c_1/c_2)$ volts. If the permeable ions cannot be assumed to follow the laws of ideal solutions, we must substitute for c_1 and c_2 the quantities termed by G. N. Lewis‡ the “activities,” or else (as is readily done) obtain an equivalent equation, involving, instead of c_1 and c_2 , the ordinary thermodynamic potentials of the ions. In the following paper an account is given of an attempt to test equation (i) by measurements of the potential difference between two aqueous solutions of potassium ferrocyanide, separated by a membrane of colloidal copper ferrocyanide.

* The experiments described in this paper were begun in October, 1911, and finished in April, 1912, their publication having been unfortunately delayed.

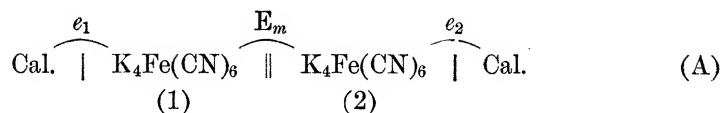
† ‘Zeitschrift für Elektrochemie,’ vol. 17, p. 572 (1911).

‡ ‘Zeitschrift für Physikal. Chemie,’ vol. 61, p. 129 (1908).

Experimental Arrangements.

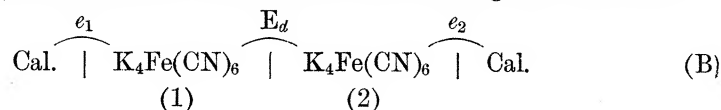
The membranes of copper ferrocyanide were made in the following way. An aqueous solution of copper sulphate of 3-per-cent. strength was separated in a suitable manner by good vegetable parchment from a 7-per-cent. aqueous solution of potassium ferrocyanide.* After three days the parchment membrane was removed, washed, and then placed in contact with the same solutions, but in reverse order, for another three days. Finally, it was taken out, well washed, and preserved under water. Parchment membranes prepared in this way proved to be quite impermeable to potassium ferrocyanide of the concentrations used in the present work.† It is necessary, however, to preserve them under water, as they gradually lose their impermeability on drying. Discs were cut from the prepared parchment and firmly fastened to glass tubes, the ends of which had been turned over to a wide and smoothly ground flat flange. The joint was made tight by Golaz cement and paraffin wax. The membrane vessel so constructed contained one of the solutions of potassium ferrocyanide and dipped into the other solution. Syphon tubes connected each solution with a vessel filled with the corresponding solution, whilst into the latter vessels dipped the syphon tubes of calomel electrodes. Great care was taken to prevent any access of potassium chloride to the solutions in contact with the membrane. The usual precautions were taken to prevent undue intermixture of the various connecting solutions. The membrane vessel, calomel electrodes, and interconnecting syphons were immersed as far as possible in the water of a thermostat, which was kept at 25°.

The determination of the membrane potential difference was carried out as follows:—The E.M.F. of the cell



(in which the calomel electrodes are indicated by the abbreviation Cal., and the membrane by the symbol ||), is constituted by the three potential differences e_1 , e_2 , and E_m , the latter being the sought-for "membrane-potential."

Suppose, now, the membrane removed and the following cell measured—



* Cf. Walden, 'Zeitschrift für Physikal. Chemie,' vol. 10, p. 699 (1892).

† In one case this impermeability was tested over a period of four months.

E_d denoting the ordinary "diffusion-potential" between the solutions (1) and (2). Then, if Δe denote the difference between the E.M.F.'s of cells A and B,

$$\Delta e = E_m - E_d,$$

and therefore

$$E_m = \Delta e + E_d.$$

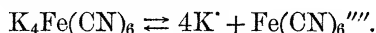
In order to determine E_m , it is therefore necessary to calculate E_d . This can be done by means of the equation

$$E_d = \frac{RT}{F} \left(u - \frac{v}{4} \right) \log \frac{\alpha_1 c_1}{\alpha_2 c_2},$$

where c_1, c_2 , are the equivalent concentrations of the two solutions of potassium ferrocyanide; α_1, α_2 , their corresponding degrees of ionisation; and u, v , the (mean) transport numbers of K and $\frac{1}{4}\text{Fe}(\text{CN})_6$. In this equation E_d denotes the excess of the positive potential of solution (2) over that of solution (1).

The values of α_1 and α_2 were taken from the conductivity data of Noyes and Johnston.*

An uncertainty, however, arises here, as this calculation assumes that the salt ionises only according to the equation



Such an assumption will be the more justified the diluter the solutions are.

A further uncertainty relates to the evaluation of u and v , since the transport numbers of potassium ferrocyanide have not been sufficiently investigated. We have therefore been obliged to calculate u and v by means of the equation $u = U/(U+V)$ and $v = V/(U+V)$, where U and V are the equivalent ionic conductivities of the potassium and ferrocyanogen ions in dilute aqueous solution at 25° . For this purpose we have taken

$$U_{\text{K}} = 74.5, \quad V_{\frac{1}{4}\text{Fe}(\text{CN})_6} = 111.0,$$

from the data of Noyes and Johnston for extreme dilution, whence follow the values

$$u = 0.404, \quad v = 0.596.$$

The values of α as determined by the work of Noyes and Johnston for the concentrations employed by us are given in the following Table, the concentrations being expressed in gramme-equivalents per litre.

Table I.—Ionisation of $\text{K}_4\text{Fe}(\text{CN})_6$ at 25° .

Concentration ...	1.0	0.1	0.05	0.04	0.02	0.0125	0.01	0.005
100 α	40	53	58.6	60.4	67.0	70.7	73.5	79.5

* Noyes, 'Amer. Chem. Soc. Journ.,' vol. 30, p. 351 (1908); Johnston, *ibid.*, vol. 31, p. 1010 (1909).

The membranes were tested to see if any potential difference existed across them when separating two solutions of potassium ferrocyanide of the same concentration. It was found that within the error of measurement no such potential difference existed.

The electromotive force was measured by means of a simple metre slide bridge and sensitive galvanometer, the precision of reading being at most 0.2 millivolt.

Contrary to expectation, constancy of electromotive force was rapidly attained and preserved over an extended period of time. This is illustrated by the following Table (time indicates duration in hours from the setting up of the cell).

Table II.—Solutions N/1 and N/10 $K_4Fe(CN)_6$.

Time.	$E_M + \Sigma e.$	$E_d + \Sigma e.$	$\Delta e.$	E_d (calc.).	$E_M = \Delta e + E_d.$
$\frac{1}{4}$	1.1198	1.0970	0.0228	0.0131	0.0359
$1\frac{1}{4}$	1.1200	1.0970	0.0230		0.0361
$2\frac{1}{4}$	1.1204	1.0970	0.0234		0.0365
$4\frac{1}{4}$	1.1207	1.0970	0.0237		0.0368
$5\frac{1}{4}$	1.1207	1.0970	0.0237		0.0368
25	1.1205	1.0970	0.0235		0.0366
27	1.1201	1.0970	0.0231		0.0362
28	1.1203	1.0970	0.0233		0.0364
29	1.1203	1.0970	0.0233		0.0364
32	1.1205	1.0970	0.0235		0.0366

It will be seen that the variation of E.M.F. observed is well within the error of measurement.

The following Table contains the experimental results, concentrations being given as before in gramme-equivalents per litre.

Table III.—Experimental Data, 25°.

Concentrations in apposition.	$E_M + \Sigma e.$	$E_d + \Sigma e.$	$\Delta e.$	E_d (calc.).	$E_M (= \Delta e + E_d).$
	volts.	volts.	volt.	volt.	volt.
N 0.1 N	1.1207	1.0970	0.0237	0.0132	0.0369
N 0.05 N	1.1323	1.1012	0.0311	0.0171	0.0482
N 0.02 N	1.1508	1.1064	0.0444	0.0222	0.0666
N 0.01 N	1.1636	1.1111	0.0525	0.0262	0.0787
0.1 N 0.05 N ...	1.0886	1.0776	0.0110	0.0039	0.0149
0.1 N 0.04 N ...	1.0917	1.0773	0.0144	0.0051	0.0195
0.1 N 0.02 N ...	1.1053	1.0808	0.0245	0.0090	0.0335
0.1 N 0.0125 N	1.1144	1.0838	0.0306	0.0117	0.0423
0.1 N 0.01 N ...	1.1176	1.0839	0.0337	0.0129	0.0466
0.1 N 0.005 N	1.1294	1.0894	0.0400	0.0170	0.0570

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The next Table shows the comparison between the values of E_M as determined in the manner explained and as calculated from equation (i).

Table IV.—Comparison of Results, 25°.

Concentrations in apposition.	E_d .	E_M from Table III.	E_M from Equation (i).	Difference.
				per cent.
N N/10	0·0132	0·0369	0·0519	28·9
N N/20	0·0171	0·0482	0·0671	28·2
N N/50	0·0222	0·0666	0·0872	23·6
N N/100	0·262	0·0787	0·1026	23·3
N/10 N/20	0·0039	0·0149	0·0152	2·0
N/10 N/25	0·0051	0·0195	0·0201	3·0
N/10 N/50	0·0090	0·0335	0·0353	5·1
N/10 N/80	0·0117	0·0423	0·0459	7·8
N/10 N/100	0·0129	0·0466	0·0507	8·1
N/10 N/200	0·0170	0·0570	0·0665	14·3

The fifth column in Table IV gives the differences between values of E_M contained in columns 3 and 4 expressed as percentages of the values given in column 4.

There is a large and fairly constant percentage deviation in all the measurements involving the equivalent normal solution of potassium ferrocyanide. Undoubtedly a large part of this must be ascribed to great uncertainty as to the correct values of the transport numbers and the degree of ionisation of this relatively strong solution. In the measurements involving no solution stronger than N/10 (lower portion of Table IV), there is a better agreement, though there is undoubtedly a tendency for the percentage deviation to increase as the ratio of dilution increases. In the case of the pairs N/10 || N/20, N/10 || N/25, and N/10 || N/50, the percentage deviation is not more than would be expected from the errors of measurement. On referring to Table III it will be seen that the percentage deviation increases as the proportion that E_d plays in the determination of E_M ($E_M = \Delta e + E_d$) increases. It seems probable, therefore, that a large part of the deviation is to be ascribed to uncertainty in the calculation of E_d .

It must also be remembered that even if the values of E_d were accurately known there might still occur deviation due to uncertainty as to the degree and nature of the ionisation of the potassium ferrocyanide and to deviation from the laws of ideal solution. Taking these various points into consideration, it seems very probable that the potential difference between two

aqueous solutions of potassium ferrocyanide separated by a membrane of colloidal copper ferrocyanide is given by the equation—

$$\pi_2 - \pi_1 = \frac{RT}{F} \log \frac{a_1}{a_2}, \quad (\text{ii})$$

where a_1 and a_2 are the “activities” of the potassium ion in the two solutions. It will be observed that equation (ii) reduces to equation (i) when the concentrations of the potassium ions are proportional to their activities.

Morphological Studies of Benzene Derivatives. VI.—*Para-sulphonic Derivatives of Chloro-, Bromo-, Iodo-, and Cyanobenzene.*

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The compounds described in this communication were examined in order to contrast the para-mono-derivatives of benzenesulphonic acid with the di-derivatives studied by Colgate and Rodd.* It is unnecessary to describe the methods used in preparing them, as these are well known.

The melting points of the various compounds are given in the following Table :—

1	4				
	SO ₂ Cl	SO ₂ Br	SO ₂ NH ₂	SO ₂ NH.Ph	SO ₂ NH.C ₆ H ₄ .CH ₃
Cl.....	53·5°	56°	143·5°	104°	87°
Br	74·5	77	165	118	94
I	84	97	190	143	129
CN	109	—	167	—	—

It is noticeable that the substitution of one halogen for another in the sulphonic radicle makes but a small difference in the melting point (about 3°) in comparison with that produced (about 20°) by a similar substitution in the nucleus.

In the case of the sulphochlorides and of the sulphonamides, the

* These Studies.—Part II, ‘Chem. Soc. Trans.’ 1910, p. 1585.